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Excited state properties of some substituted pyridine and benzenes using solvatochromic shift

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Abstract : From the solvatochromic shift of the absorption bands of eight symmetrically substituted benzene and four substituted pyridine molecules in different solvents, the excited state dipole moment and the position of absorption maximum in vapour phase have been calculated on the basis of non-specific solute-medium interactions. Considering the good agreement between measured and calculated values of the position of absorption band in vapour phase (ν_v), this method may be utilized to find ν_v in the case of symmetry or otherwise forbidden transitions. The shape parameter of the cavity in which the solute molecule lies, has been determined and used to identify the direction of photoabsorption

Keywords : Solvatochromic shift, excited state, dipole moment, shape parameter.

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1. Introduction

The understanding of the nature and energy of electronically excited states in condensed or liquid phases, is of paramount importance in delineating the different photophysical and photochemical processes of a molecule. The solvatochromic shifts, related to non-specific solvent-solute interactions are the experimental evidence about the stabilisation of energy states in solvents and they have been used in determining excited state properties [1-12]. The excited state dipole moment gives an understanding of the electron distribution change in such state and also indicates a possibility of charge transfer character of the electronic transition. In ground state, the symmetrically substituted aromatic molecules can have no dipole moment, unless there is a significant distorsion which breaks the symmetry and also some of them have forbidden transitions. In this paper, we report the excited state dipole moment, position

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of excited state in vapour phase and the shape of the cavity in which the solute molecule lies in the solvent for a series of symmetrically substituted benzene molecules and substituted pyridines, from the solvatochromic shifts.

2. Experimental

The samples p-dimethoxybenzene (DMB), 1,3,5-trimethoxybenzene (TMB), p-diiodobenzene (DIB), p-dibromobenzene (DBB), 1,3,5-trichlorobenzene (TCB), 1,3,5-tribromobenzene (TBB), 1,2,4,5-tetrachlorobenzene (TTCB) and hexachlorobenzene (HCB) were obtained from Fluka AG, and 2-, 3- and 4-phenylpyridine (2PhPy, 3PhPy, 4PhPy) and 2,6-diphenylpyridine (DPP) were purchased from Aldrich chemical co., Inc. DPP, DBB, TBB, TCB and the phenylpyridines were sublimated several times under reduced pressure before use. DIB, DMB, TMB, TTCB, and HCB were recrystallised from ethanol to get pure samples. The spectroscopic grade solvents cyclohexane (CH), carbontetrachloride (CTC), benzene (BZ), n-pentane (NP), n-heptane (NH), iso-octane (IO), methylcyclohexane (MCH), n-butylalcohol (NBA), isobutylalcohol (IBA), tetrahydrofuran (THF), and chloroform (CF) were obtained from E. Merck. The UV absorption spectra of all molecules in polar and nonpolar media (C ~ 10^{-5} to 10^{-4} M) have been taken with Shimadzu UV-VIS Absorption Spectrophotometer model 210A.

The ground state dipole moment (μ_g) of all the molecules have been taken from the literature and only that of DPP was measured in p-xylene solution using the relation

$$\mu_g^2 = 9kT(\varepsilon_s - \varepsilon_\alpha)(2\varepsilon_s + \varepsilon_\alpha)\Big/\left[4\pi N_1 \varepsilon_s (\varepsilon_\alpha + 2)^2\right]$$

where, N_1 = no. of solute molecules per c.c. of the solution, k = Boltzman's constant, T = absolute temperature, ε_s = static dielectric constant of the solution measured as the ratio of capacitance of the solution to the capacitance of air, and ε_α = infinite frequency dielectric constant $\simeq n^2$ (n = refractive index of the solution).

The capacitance was measured with a General Radio Capacitance Bridge, model 1615A. The refractive indices of solutions of various concentrations were measured with the help of Abbe's refractometer. The dipole moment at infinite dilution was measured from extrapolation of the curve of dipole moment *versus* concentration plot, to get the value of ground state dipole moment for isolated DPP molecule. The refractive indices and dielectric constants of the solvents used for the measurement of solvatochromic shifts were taken from the literature [13].

3. Results and discussion

For a series of nonpolar solvents of different refractive indices the well known McRae's equation [14] relating to solvent induced shift of electronic absorption bands may be written [15,16] as

$$-\Delta\upsilon_{1-2} = \left(\mu_g.\Delta\mu_{g,e}\right)\left\{\Delta\left[f(D) - f(n^2)\right]_{1-2}\right\}\Big/hca^3 + \left(\mu_e^2 - \mu_g^2\right)\Delta f(n^2)_{1-2}\Big/2hca^3, \quad (1)$$

where $\Delta\nu_{1-2}$ signifies the frequency shift of a particular absorption band between solvent 1 and 2 ; μ_g and μ_e are the ground state and excited state permanent dipole moment respectively; $\Delta\mu_{g,e}$ is the change in permanent dipole moments between ground and excited states; a is the radius of cavity occupied by each solute molecule in the solvent of dielectric constant D. The functions $f(D)$ and $f(n^2)$ are defined as

$$f(D) = 2(D - 1)/2D + 1 \text{ and } f(n^2) = 2(n^2 - 1)/2n^2 + 1.$$

In relation (1) it is assumed that the molecular volume does not change appreciably on excitation and the shape of the molecules are spherical. Besides these, the dipoles μ_g and μ_e are assumed to be centered at the same point in the molecule. The dot product in relation (1) may be simplified as

$$\mu_g.\Delta\mu_{g,e} = \mu_g.(\mu_g - \mu_e) = [\mu_g]^2 - [\mu_g][\mu_e]\cos\theta$$

where θ is the angle between the vectors μ_g and μ_e.

For nonpolar solvents ($n^2 \simeq D$) of different refractive indices, the relation (1) reduces to

$$-\Delta\nu_{1-2} = \left(\mu_e^2 - \mu_g^2\right)\Delta f(n^2)_{1-2}/2hca^3. \tag{2}$$

Considering the high percentage of error in the measurement of small frequency shift $\Delta\nu_{1-2}$, we take vacuum as reference [$n = 1$; $f(n^2) = 0$] and the eq. (2) may be written as

$$\nu_s = \nu_v - \left(\mu_e^2 - \mu_g^2\right)f\left(n_s^2\right)/2hca^3, \tag{3}$$

the subscripts s and v refer to solution and vapour phase respectively.

Again for a series of solvents having almost same refractive indices but different dielectric constants, Suppan and Tsiamis [3] showed that the relation (1) takes the form

$$-\Delta\nu_{1-2} = \mu_g.\Delta\mu_{g,e}\,\Delta f(D)_{1-2}/hca^3. \tag{4}$$

Now it is clear from (3) that for a set of nonpolar solvents with different refractive indices, a plot of ν_s (absorption maximum of $S_1 \leftarrow S_0$ or $S_2 \leftarrow S_0$ of a solute molecule against $f(n^2_s)$ would give a straight line with negative slope $(\mu_e^2 - \mu_g^2)/2hca^3$ and the intercept on frequency axis would give us the absorption maximum in vapour phase. Knowing the Onsagar cavity redius a and μ_g, one can find out the value of μ_e. Dipole moments determined in this way are those of Franck-Condon excited states. μ_e of FC state is the measure of asymmetry of the electrical charges of the solute molecule under the influence of surrounding solvent dipoles. The slope or the specific shift $(hc\Delta\nu/\Delta f(n^2))$ arises due to the following three reasons :

(1) dispersion effect, arising due to the interaction between two nonpolar, polarizable solute and solvent molecules;

(2) interaction between solute dipole and solvent polarizability;

(3) transition dipole moment term which describes the motion of electrical charges during transition.

For solute having large μ_g, the dispersion and transition moment term is negligible compared to dipole-polarizability interaction term. But the molecules with small μ_g, can have high transition dipole moment and dispersion effect which are not negligible compared to the small interaction between total dipole moment of solute and induced dipole moment of polarizable solvent. So the specific shift obtained in these cases are the measure of the sum of above mentioned three quantities and the calculation of μ_e from this specific shift will be erroneous until we subtract the dispersion and transition dipole moment term from it. A similar plot of ν_s in different solvents having approximately same refractive index but different dielectric constants, *versus* corresponding $f(D_s)$ will give another straight line with a negative slope of $\left(|\mu_g|^2 - |\mu_g||\mu^e|\cos\theta\right)/hca^3$ and a previous knowledge of μ_e will give us the value of angle θ between μ_g and μ_e.

In finding the value of μ_e and θ we calculated the value of a, by the method of atomic increments [17], assuming the molecules to be spherical in shape. But actually each solute molecule is surrounded by the solvent molecules in an ellipsoidal cavity, whose geometrical shape depends on that of solute molecules. For the sake of simplicity, it is assumed that the photoabsorbing transition of the solute molecule takes place along one of the three principal axes of the ellipsoidal cavity. So, to get an idea about the shape of the cavity, in which the solute molecule is supposed to lie, we have calculated the shape parameter s of the cavity, using the equation proposed by Shibuya [18]

$$(nf'')^{0.5} = s(n^2 - 1)f^{0.5} + f^{0.5}$$

where f'' is the oscillator strength [19] of a nonpolar molecule measured in a nonpolar solvent of refractive index n and f is the oscillator strength of the solute molecule in vacuum. A plot of $(nf'')^{0.5}$ against (n^2-1) gives the values of f and s. The shape parameter s is identified with the depolarisation factor of a dielectric in the same shape as the cavity for the direction of the transition moment.

The values of μ_e, μ_g, θ, ν_v, f and s have been presented in Table 1. Assuming a planar configuration, the ground state dipole moment of DPP calculated from bond dipoles [20,21] is 2.23 D. The measured value of μ_g for DPP is 2.29 D (Table 1) which confirms the planarity of the molecule in the ground state. From the table it is found that the molecules DMB, TMB, DPP and phenyl pyridines acquire reasonably high dipole moment in the excited state with respect to ground state, which gives an indication of nonsymmetric nature of charge distribution in the excited FC state.

In the case of nonpolar molecules *i.e.* with insignificant value of μ_g, the angle θ have intentionally not been computed because in these cases, the specific shift $(hc\Delta\nu/f(D))$ arises mainly due to the 'solvent Stark effect', and the dipole induced dipole term is practically zero. It is unfortunately impossible to separate these two contributions.

Table 1. Excited state dipole moment *etc* for different molecules.

Name of the sample	Onsagar radius (A°)	μ_g^a (Debye)	λ_{max} (nm)	in vapour state (cm^{-1}) ν_{max} present work	ν_{max} other work	specific shift (cm^{-1})	μ_e (Debye)	θ (Degree)	f	s
DMB	3.2	1.70	299.0	33951 ± 14	33840[c]	2776 ± 71	4.0 ± .05	66	4.3×10^{-2}	0.35
TMB	3.3	1.80	265.8	38413 ± 34	–	5143 ± 175	6.0 ± .11	78	8.5×10^{-3}	0.06
HCB	3.5	0.20	299.8	33948 ± 20	–	3122 ± 102	–	–	2.2×10^{-1}	0.45
TTCB	3.3	0.06[b]	294.4	34319 ± 10	34149[d]	1786 ± 53	-	-	1.3×10^{-2}	0.19
TCB	3.2	0.28	280.8	35669 ± 6	35498[e]	465 ± 30	–	–	1.5×10^{-1}	0 32
TBB	3.3	0.28	282.8	35503 ± 8	–	789 ± 42	–	–	2.5×10^{-1}	0.76
DBB	3.1	0.0	282.3	35856 ± 11	35751[f]	2272 ± 56	–	–	3.6×10^{-3}	0.12
DIB	3.3	0.19	278.0	36393 ± 20	–	2040 ± 103	–	–	1.3×10^{-2}	0 51
DPP	3.8	2.29	301.5	33479 ± 10	33868	1763 ± 52	4.9 ± 06	74	0 15	0.38
2PhPy	3.3	1.94	274.5	37097 ± 16	–	3468 ± 83	5.4 ± 05	47	0.50	0.15
3PhPy	3.3	2.45	243.5	42140 ± 28	–	5570 ± 144	6.8 ± .07	34	0.46	0.19
4PhPy	3.3	2.57	247.0	41582 ± 38	–	5641 ± 194	6.9 ± .10	88	0 12	0.80

[a]Ref. [23] ; [b]Ref. [24] ; [c]Ref. [25] ; [d]Ref. [26] ; [e]Ref. [27] ; [f]Ref. [28].

Estimation of vibronic maximum in the vapour phase of molecules from the solvatochromic shift [relation (3)] is interesting and important, specially for the molecules which have symmetry or otherwise forbidden electronic transitions. The values of ν_v of the molecules have been shown in Table 1 and they are in reasonably good agreement with the reported experimental values (deviation within 1%) in vapour phase. In general, the calculated values are greater than those of the measured values [4].

The last column of Table 1 reports the values of shape parameter for all the molecules. It seems that in the case of most of the molecules, the shape of the cavity is a sphere or near to it. Ideally, where the cavity of the solute molecule is spherical, the photoabsorption occurs in any direction and the value of $s = 0.33$. For HCB and DIB, the transition occurs in the transverse direction of a long cylindrical cavity (ideal value of $s = 0.50$). The transition moment of TMB may be considered to be in the longitudinal direction of a long cylinder or in the plane of a thin slab cavity ($s = 0$) [11,18,22].

4. Conclusion

From the foregoing discussion, it is clear that the estimation of vibronic maximum in vapour phase from solvatochromic shift is very important specially in the case of symmetry forbidden transitions. The idea of the shape of the cavity has been used in predicting the direction of photoabsorption and the increase in dipole moment from ground to first excited singlet state in some cases, has been associated with the asymmetry or change in electron distribution of the solute molecule.

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